

10/537,693

PTO 07-3616

PN=S62-24244
CY=JP
DATE=19870202
KIND= A

SILVER HALIDE PHOTOGRAPHIC-SENSITIVE MATERIAL
[□□□□□□□□□□]

SAKAMOTO HIDEKAZU et al.

UNITED STATES PATENT AND TRADEMARK OFFICE
Washington, D.C. April, 2007

Translated by: Linguistic Systems, Inc.

PUBLICATION COUNTRY	(10): JP
DOCUMENT NUMBER	(11): 57205458
DOCUMENT KIND	(12): A
PUBLICATION DATE	(43): 19870202
APPLICATION NUMBER	(21): S62-24244
APPLICATION DATE	(22): 19850724
INTERNATIONAL CLASSIFICATION	(51): G03C 1/34
PRIORITY COUNTRY	(33): N/A
PRIORITY NUMBER	(31): N/A
PRIORITY DATE	(32): N/A
INVENTOR	(72): SAKAMOTO HIDEKAZU et al.
APPLICANT	(71): KONISHIROKU PHOTO INDUSTRIES CO LTD
TITLE	(54): SILVER HALIDE PHOTOGRAPHIC-SENSITIVE MATERIAL
FOREIGN TITLE	[54A]: □□□□□□□□

- (19) JAPANESE PATENT OFFICE (JP)
(11) Unexamined Patent Application (Kokai) Patent S62-24244
(12) Official Gazette for Kokai Patent Applications (A)
(43) Publication Date: February 2, 1987

(51) Int. Cl. ⁴	Identification Symbol	JPO File No.	FI	Tech. Ind.
G03C 1/34		7915-2H		
//C 07 D 235/04		7166-4C		
235/22		7166-4C		

Number of inventions: 1 Total Number of Pages: 20

(54) Title of the Invention SILVER HALIDE PHOTOGRAPHIC-SENSITIVE MATERIAL

Request for Examination: No

(21) Application No.: S60-164875

(22) Filing Date: July 24, 1985

(71) Applicant KONISHIROKU PHOTO INDUSTRIES CO LTD

(72) Inventors SAKAMOTO HIDEKAZU et al.

SPECIFICATION

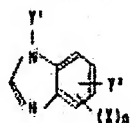
1. Title of the Invention

SILVER HALIDE PHOTOGRAPHIC-SENSITIVE MATERIAL

2. Claims

A silver halide photographic-sensitive material that contains a silver halide emulsion layer or at least one kind of a compound that is expressed by general formula [I] in an adjacent layer.

General formula [I]



(Within the formula, Y1 expresses a hydrogen atom, R1, -COR2 or -SO₂R3, R1, R2, and R3 express every aliphatic or aromatic groups. Y2 expresses a hydrogen atom, -NHR4, -NHCOR5 or -NHSO₂R6, R4, R5, and R6 express every aliphatic and aromatic group, and R4 expresses also a hydrogen atom. However, Y1 and Y2 are not hydrogen atoms at the same time, and when R4 is a hydrogen atom, Y1 is R1, -COR2 or -SO₂R3. Furthermore, X expresses a halogen atom, alkyl radical, aryl radical, alkoxy radical, hydroxyl radical, and nitro radical or cyan radical, n denotes 1 or 2)

3. Detail Description of the Invention

[Industrial Field of the Invention]

This invention is related to a silver halide photographic-sensitive material, and especially to a silver halide photographic-sensitive material where there is temporary generation of capry in the photosensitive material.

(Prior Art)

Silver halide photographic-sensitive material has the

tendency to generate capry caused by the existence of fragments that are not exposed, and especially, extremely often a reduction in sensitivity occurs with the generation of capry that temporarily exists, and extremely often this condition invites tone deterioration.

Because it is desirable to minimize as much as possible this kind of undesirable phenomenon, it has been conventional practice to add a capry inhibitor or stabilizer to a silver halide emulsifier. As disclosed in US Patents 2, 403, 927, 3,804, 633, and Japanese Patent S39-2825, 1-phenol-5-mercapto tetrazoil or 4-hydroxy-6-methyl-1, 3, 3a, 7-tetrazaidine has been used as a capry control agent.

However, the control effect of these compounds for temporarily existing capry has not necessarily been sufficient, and the shortcomings of reduced sensitivity and tone softening do not produce a satisfactory result.

In addition, when using color photosensitive material, the capry control agent used for improvement exists temporarily and is strongly absorbed, more than necessary, by the silver halide emulsifier, and it causes much damage through its sometimes delaying desilvering during image processing.

[Goal of the Invention]

Consequently, in view of the shortcomings mentioned above,

this invention has as its first goal the prevention of deterioration of the photographic performance while temporarily existing in the silver halide photographic-sensitive material by providing a silver halide photosensitive material that controls capry generation. The second goal of the invention is to provide silver halide photographic-sensitive material that contains a capry control agent for which there is little fear of sensitivity reduction or tone weakening from image development control.

The third goal of this invention is to provide a silver halide photographic-sensitive material for image properties that are stabilized without any image development controls based on control agents that dissolve during image development of the photosensitive material.

The fourth goal of this invention is to provide a silver halide photosensitive material for which capry generation is controlled and no damage is done to desilvering with color image development processes.

[Constitution of the Invention]

The previously mentioned goals of the present invention are achieved by silver halide photosensitive material that contains a silver halide emulsion layer or at least one kind of compound that is expressed by the following

equation [I] within its adjacent layer.

General formula [I]

(Within the formula, Y1 expresses a hydrogen atom, R1, -COR2 or -SO₂R3, R1, R2, and R3 express every aliphatic or aromatic group. Y2 expresses a hydrogen atom, -NHR4, -NHCOR5 or -NHSO₂R6, R4, R5, and R6 express every aliphatic and aromatic group, and R4 expresses also a hydrogen atom. However, Y1 and Y2 are not hydrogen atoms at the same time, and when R4 is a hydrogen atom, Y1 is R1, -COR2, or -SO₂R3. Furthermore, X expresses a halogen atom, alkyl radical, aryl radical, alkoxy radical, hydroxyl radical, and nitro radical or cyan radical, (n denotes 1 or 2).

Below, there are details of the present invention.

In the above equation [I], aliphatic groups expressed by R1-R6 are desirable as alkyl groups of carbon number 1-8 (especially 1-6), alkoxy groups of carbon number 1-8 (especially 1-6), and alkenyl groups of carbon number 3-8 (especially 3-4).

Those having the alkyl group, alkoxy group, and the alkenyl group are included, and as desirable substitution groups, there are the hydroxyl groups, cyano groups, alkoxy groups, alkoxycarbonyl group, carboxy group (contains alkali metal salts and ammonium salts), and sulfo group (contains alkali metal salts and ammonium salts).

More specifically, there can be cited for the alkyl group of the alkyl group and alkoxy group mentioned above the following: an ethyl group, butyl group, hydroxymethyl group, hydroxyethyl group, cyanoethyl group, carboxyethyl group, sulfopropyl group, and benzyl group.

There can be cited for the alkenyl group mentioned above the following alkyl group, butenyl group, hexenyl group, 4-carboxy-2-butenyl group, and 6-hydroxy-2-hexenyl group.

In addition, for the aromatic group, the aryl group is desirable, and for the aryl group, there is the phenyl group and the naphthyl group, and among the aryl groups, phenol groups.

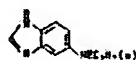
The aryl group contains substances that have substitution groups, and as desirable substitution groups, there can be cited the following: alkyl groups of carbon atom number 1-8 (more preferably 1-6), for example, the methyl groups and ethyl groups; halogen atoms, for example, chlorine atoms, iodine atoms; nitro groups; carboxy groups (contains alkali metal salts and ammonium salts); alkoxy carbonyl groups; and sulfo groups (contains alkali metal salts and ammonium salts).

The halogen atoms that are expressed by X are, for example, chlorine atoms or iodine atoms, and the alkyl groups are lower-level alkyl groups of carbon number 1-4 (for example,

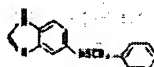
methyl groups, ethyl groups), and the aryl groups are, for example, phenol groups, and the aralkyl groups are, for example, the benzoyl groups, and alkoxy groups are methoxy or ethoxy groups.

Next, there are shown concrete examples that are used for the present invention, but the present invention is not limited to these.

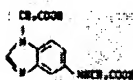
(1)



(2)



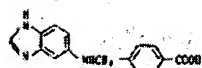
(3)



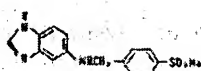
(4)



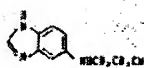
(5)



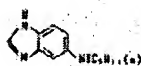
(9)



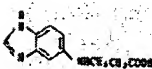
(6)



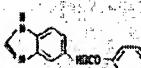
(10)



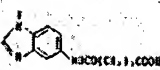
(7)



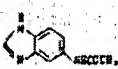
(11)



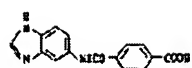
(8)



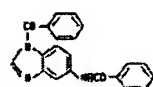
(12)



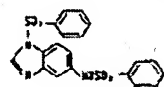
(13)



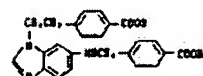
(14)



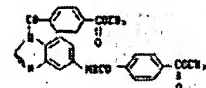
(15)



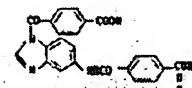
(16)



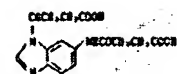
(17)



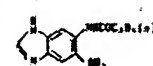
(18)



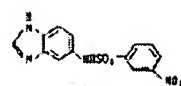
(19)



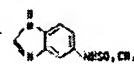
(20)



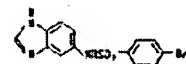
(17)



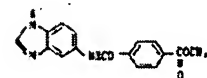
(18)



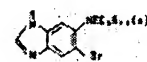
(19)



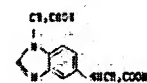
(20)



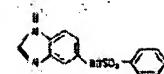
(21)



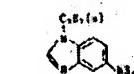
(22)



(23)



(24)



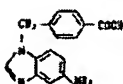
(29)



(30)



(31)



(32)



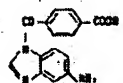
(37)



(38)



(39)



(40)



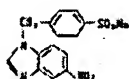
(23)



(34)



(35)



(36)



(41)



(42)

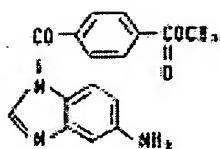


(43)



(44)





The compounds that are expressed by general formula [I], which is related to the present invention, for example, can be easily synthesized by a method contained in Klave Hofmann's Imidazole and Its Derivatives Part I (1975) p. 253 (The Chemistry of Heterocyclic Compounds), and in Bulk Organic Chemistry 15, Complex Heterocyclic Compounds II, by Otake and Tada (1958) p. 238.

Synthesis Example-1 (Synthesis of illustrated compound 8)
Dissolve in 100ml of acetic acid 5-amino benzoimidazole 13.3g and continue stirring as is. Add for 3 minutes at room temperature anhydrous succinic acid 9.0g that was dissolved in 50ml of ethyl acetate, and after dissolving, continue to stir for 30 minutes, and afterwards, a white powder crystal precipitates. Taking the precipitated crystal, obtain the desired substance of 10.5g by recrystallizing using 80% methanol aqueous solution. The mass spectrum and the nuclear magnetic resonance spectrum (NMR spectrum) support the structure of the illustrated compound 8.

Synthesis Example-2 (Synthesis of illustrated compound 15)

Dissolve in pyridine 100ml 5-aminobenzoimidazole 13.3g and continue stirring as is. After adding for 10 minutes at room temperature 36g of benzenesulfonyl chloride, continue to stir for 2 hours.

Afterwards, put reaction liquid in 400ml of ice water take out the precipitated crystal and obtain a white-colored powder crystal 20g by recrystallizing with methanol.

The mass spectrum and the nuclear magnetic resonance spectrum (NMR spectrum) support the structure of the illustrated compound 15.

Synthesis Example-3 (Synthesis of illustrated compound 27)

Dissolve in 100ml of methanol 19g of the illustrated compound 15 that was obtained using Synthesis Example-2 and continue stirring as is. Drip for one hour at room temperature 60ml of a 10% sodium hydroxide solution.

Afterwards, after continuing to stir for an additional 30 minutes, if the acidity of the reaction liquid is adjusted with dilute hydrochloric acid, crystal will precipitate.

Take the crystal and after repeated washings obtain a white powder crystal 5.5g by recrystallizing using 80% methanol aqueous solution.

The mass spectrum and the nuclear magnetic resonance spectrum (NMR spectrum) support the structure of the illustrated compound 27.

The compound of the present invention contains a silver halide emulsifier layer of silver halide photographic material and at least one layer of a formed layer that is established by common photosensitive material such as an intermediate layer that is adjacent to the halide layer, a filter layer, a halation prevention layer, and an undercoat layer. An especially desirable layer is the silver halide emulsifier layer.

The amount of the compound in the present invention is suitable at silver halide 1-1000mg per mole, especially desirable at 10-700mg, and it is suitable to have 0.1mg-2g per 1 m² of support for the layers other than the silver halide emulsifier layer, which is especially desirable in the range of 1mg-1g. In addition, it is desirable that the additions periods before emulsifier coating be when adding the silver halide emulsifier, during chemical thermoforming, after completion of the chemical thermoforming, and/or after completion of the chemical thermoforming. It is more desirable after completion of chemical thermoforming of the silver halide emulsifier. The compound of this present invention can be used with

well-known capry inhibitors other than the compounds already listed.

For the present invention's silver halide emulsifier, it is possible to use substances that are used for common silver halide emulsifiers, such as silver bromide, silver iodine bromide, silver iodine chloride, silver chlorine iodine, and silver chloride.

The silver halide particles that are used in the silver halide emulsifier may be obtained by any method, such as an acid process, neutral process, or ammonia process. The particle may be temporarily developed and may be formed after developing any type of particle. The method that makes the particle and the method that grows it may be different.

Silver ions and halide substance ions may be mixed at the same time for the silver halide emulsifier, and may be mixed using a method that is different from the one that places the emulsifier in solution. In addition, considering the critical growth rate of the silver halide crystals, development is permissible by adding simultaneously while controlling the pH or pAg within the mixing pot for the halide substance ions and the silver ions. By this method,

silver halide particles are obtained that are nearly uniform in size, with a regulated crystal form. By using a compaction method after formation, the halogen composition of the particles may be changed.

The silver halide emulsifier, using a silver halide solution as necessary during preparation, can control the particle size of the silver halide particles, the shape of the particles, the particle size distribution, and the development rate of the particles.

There is added at least one kind of metal ion that is selected from, for the silver halide particle, in the process that forms the particles and/or grows them, cadmium chloride, zinc chloride, copper chloride, titanium chloride, iridium chloride (containing a complex salt), rhodium chloride (containing a complex salt), and iron chloride (containing a complex salt), and it is possible to contain metal elements of these within the particles and/or on the particle surface, and by leaving the particles in an appropriate reducing atmosphere, it is possible to give a reduced increased sensitive core to within the particle and/or on the particle's surface.

Elimination of unnecessary soluble salts may be made for the silver halide emulsifier after growth of the silver halide particles, or the salts may remain. When eliminating

the salt deposits, it is possible to perform the elimination based on a method contained in Research Disclosure (hereafter, abbreviated as RD) 17643 II page. The silver halide particles have a uniform silver halide distribution within the particles, and within the particles and on the surface there may be core/shell particles whose silver halide composition is different. The silver halide particles may be particles so as to cause latent images to be mainly formed on the surface, and mainly formed within the particles. The silver halide particles may have a regular crystalline shape such as a cube, octahedral shape, or decahedron, and may have a spherical or plate-like irregular crystalline shape. It is possible to use an arbitrary number for the ratio of the {100} surface and {111} surface. In addition, there may be complex shapes for these crystal forms, and it is possible to mix particles of various crystalline shapes. The silver halide emulsifier is made by using particles of any size distribution. Emulsifiers (abbreviated as multiple dispersion emulsifiers) of wide particle size distribution may be used, and emulsifiers (abbreviated as single dispersion multipliers) may be used. Here, for the single dispersion emulsifier, when dividing the standard

difference by a uniform particle diameter, the value is said to be 0.20 or less. Here, the particle diameter, when using a spherical-shaped silver halide particle, the diameter is shown, and when it is a particle of non-spherical shape, the diameter (when converting the projected image for a circular image of equal surface area) with narrow particle size distributions may be used independently or as blends of several kinds. In addition, mixing may be done of multiple dispersion emulsifiers and single dispersion emulsifiers.

The silver halide emulsifier may be used by mixing 2 or more kinds of silver halide emulsifiers that have been separately formed.

The silver halide emulsifiers may undergo chemical sensitization by normal methods. That is, the following methods may be used independently or in combinations: sulfate sensitization, selenium sensitization, reducing sensitization, and precious metal sensitization that uses silver and other precious metal compounds.

The silver halide emulsifier, using pigment that is known as a sensitizing color in the photography industry, can optically sensitize in a desired wavelength region. The sensitizing pigment may be used independently or in combinations of 2 or more kinds. Together with the

sensitizing pigment, there is a pigment that does not support itself the use of spectral sensitization or a compound that does not substantially absorb visible light and may contain within the emulsifier a strong pigment sensitizer that enhances sensitization use of sensitizing pigments.

The following have been cited for the sensitizing pigment: cyano pigment, melocyan pigment, complex cyan pigment, complex melocyan pigment, holopolar cyan pigment, hemicyan pigment, steryl pigment, and hemioxanol cyan pigment.

The pigments that are especially used are the cyan pigment, melcyan pigment, and the complex melocyan pigment. These pigments can be used with any of the nuclei that are normally used in cyan pigment types as a basic heterocyclic nucleus. That is, pyrroline nucleus, oxzoline nucleus, thiazoline nucleus, pyrrol nucleus, oxzol nucleus, thiazole nucleus, selenazol nucleus, imidazole nucleus, tetrazol nucleus, pyridine nucleus, and nuclei that have fused fats expressed as hydrocarbons with these nuclei, indolene nucleus, benzoindolene nucleus, indole nucleus, benzooxazol nucleus, naphthoxazol nucleus, benzothiazol nucleus, naphthothiazole nucleus, benzoselenazole nucleus, benzoimidazol nucleus, quinolene nucleus, etc. These nuclei may be replaced by carbon atoms.

The following can be used as a nucleus that has a keto-methylene structure in melocyan pigment or complex melocyan pigment: 5-6 member heterocyclic nuclei such as pyrrazoline-5-on nucleus, thiohydantoin nucleus, 2-thioxazoline-2, 4-dion nucleus, thiazolidine-2, 4-dion nucleus, rhodanine nucleus, and [UNKNOWN].

The following have been cited as containing recommendations for sensitizing pigments that can be employed in a useful blue light sensitive silver halide emulsifier layer (all references are to US Patent numbers):

本國特許 2,231,858 号、同 2,493,748 号、同 2,503,776 号、同 2,519,001 号、同 2,912,329 号、同 3,856,859 号、同 3,872,897 号、同 3,894,217 号、同 4,025,349 号、同 4,046,372 号、英國特許 1,242,588 号、特公昭 44-14030 号、同 52-24844 号に記載され

In addition, it is possible to cite as replacements cyan pigment, melocyan pigment, or complex cyan pigment, which are contained in the following US Patents:

同 2 号 英國特許 1,939,201 号、同 2,072,908 号、同 2,739,149 号、同 2,946,763 号、本國特許 505,979

Furthermore, the cyan pigment, melcyan pigment, or complex cyan pigment that may be used as a replacement for a beneficial sensitizing pigment in red light sensitive

silver halide emulsifiers can be cited in US Patents 2, 269, 234, 2, 270, 378, 2, 442, 710, 2, 454, 629, and 2, 776, 280. In addition, the same can be said for the cyan pigments, melcyan pigments, or complex cyan pigments contained in US Patents 2,213,995, 2, 493, 748, 2, 519,001, and German Patent 929,080.

These sensitizing pigments can be used independently but may also be used in combinations. The combinations of the sensitizing pigments are often used as strong color sensitizers. Representative examples can be found in the following Japanese and US Patents:

Japanese S43-4932, S43-4933, S43-4936, S44-32753, and S45-25831 and

25831号、同45-28474号、同46-11627号、同46-
18107号、同47-8741号、同47-11114号、同47-
25379号、同47-37443号、同48-28283号、同48-
28408号、同48-33407号、同48-38488号、同48-
41203号、同48-41204号、同48-4207号、同50-
48862号、同53-12375号、同54-24533号、同55-
1565号、同56-23220号、同56-23824号、同56-
28528号、同51-107127号、同51-116320号、同51-
133528号、同51-151327号、同52-23831号、同52-
51932号、同52-184916号、同52-104917号、同52-
149925号、同52-115818号、同54-88116号、同56-
23728号、同57-1438号、58-10753号、同58-
91415号、同58-153928号、同59-114333号、同59-

and S59-116647 and US Patents:

116645号、同59-116647号、本国特許2,688,545号、
同2,977,229号、同3,397,068号、同3,508,443号、
同3,578,447号、同3,672,898号、同3,679,428号、
同3,769,301号、同3,814,609号、同3,837,862号

As for the substances that show strong color sensitizing as substances that are used together with sensitizing pigments, as pigments that do not support use in spectral sensitization, and that do not substantially absorb visible light, there are, for example, aromatic organic formaldehydes condensate (for example, the substance mentioned in US Patent 3,473,510), cadmium salt, [UNKNOWN], and amino stilbene compound, which is replaced by nitrogen-containing heterocyclic groups (for example, mentioned in US Patents 2, 933, 390, 3,635, 721). It is especially beneficial to use the US Patents 3, 615, 613; 3, 615, 641; 3, 617,295; and 3, 635,721.

The silver halide emulsifier can, during the manufacturing process of the light-sensitive material, during maintenance, and during photographic processing, prevent capry, and during chemical thermoforming, with a goal of maintaining photographic performance stability, and after thermoforming completion, until coating of the silver halide emulsifier, it can add well-known compounds in the photography world as capry inhibitors or stabilizers.

As for the capry inhibitors and stabilizers, the following are appropriate: pentazaidine types mentioned in US Patents 2,713,541; 2, 743, 180; 2, 743, 181; and tetrazaindine

types contained in 2, 716, 062; 2, 444, 607; 2, 444, 605; 2, 756, 147; 2, 835, 581; 2, 852, 375; RD 14851; azaidine types such as polymerized azaidine, which are contained in 2, 772, 164 and in Japanese Patent S57-211142; thiazolium salt, contained in US Patents 2, 131, 038; 3, 342, 596; and 3, 954, 478; pyrylium salts, which are mentioned in US Patent 3, 148, 067, and fourth level onium salt, such as phosphonium salt mentioned in 3, 148, 067, and Japanese Patent 50-40665; mercaptotetrazol types, mercaptotriazol types, and mercaptodiazol types mentioned in US Patents 2, 403, 927; 3, 266, 897; 3, 708, 303; and Japanese Patents S55-135835, and S59-71047; mercaptodiazol contained in US Patent 2, 824,001, and mercapto benzothiazol contained in 3, 397, 987; mercaptooxazdiazol, mentioned in US Patent 2, 843, 491; mercapto substitute heterocyclic compound types such as mercaptothiadiazol, contained in US Patent 3,364, 028; catechol types, contained in Japanese Patent S43-10256, resorcin, which is contained in Japanese Patent S56-44413, and polyhydroxy benzene, such as gallic acid ester, which is contained in S43-4133; tetrazol types, which are contained in German Patent 1, 189, 380; triazol types, contained in US Patent 3, 157, 509; benzotriazol types, which are contained in US Patent 2, 704, 721; ulazol types, contained in US Patent 3, 287, 135; pyrizol types,

contained in US Patent 3, 106, 467; indazol types, contained in US Patent 2, 271, 229, polymerized benzotriazol types, contained in Japanese Patent S59-90844; pyridine types, contained in US Patent 3, 161, 515; heterocyclic compound types such as 3-pyrrizolidone, contained in US Patent 2, 751, 297, and polymerized pyrrolidone, contained in US Patent 3, 021, 213; every kind of control agent precursor, contained in Japanese Patent S54-130929, S59-137945, S59-140445, English Patent 1, 356, 124, US Patents 3, 575, 699 and 3, 649, 267; sulfonic acid and sulfonic acid derivatives, contained in US Patent 3, 047, 393; and inorganic salts, contained in US Patents 2, 556, 263; 2,839, 405; 2, 488, 709; and 2, 728,663.

As for the binder (or maintenance colloid) for the silver halide emulsifier, gelatin can be beneficially used, but it is possible to use gelatin derivatives, gelatin, and other polymer graft polymers, proteins of other than those of the polymers, sugar derivatives, cellulose derivatives, and hydrophilic colloids such as synthetic hydrophilic polymer substance as single or copolymers.

The photo emulsifier layer of photosensitive material for the present invention and other hydrophilic colloid layers can be hardened by using 1 kind or 2 or more kinds of hardener that increase the hardening strength by cross-

linking binder (or protective colloid) atoms. The hardener can be mass additions, which can harden the photosensitive material to the degree that it is not necessary to add a hardener during liquid processing, but it is possible to add a hardener during liquid processing.

It is possible to add plasticizers with the goal of increasing flexibility on the silver halide emulsifier layer of the photosensitive material and/or other hydrophilic colloid layers. A desirable plasticizer is a compound contained in item XII of RD17643.

It is possible, in the silver halide photosensitive material and other hydrophilic colloid layers, to have aqueous non-solubility or dispersed substances of hard-to-dissolve synthetic polymer dispersed substance (latex).

A pigment-forming coupler is used on the emulsifier layer of the photosensitive material. This coupler performs a coupling reaction with an oxide of aromatic primary amine developer (for example, p-phenylene diamine derivative or amino phenol derivative) in the color generating image process. The selection is ordinary, so as to form a pigment that absorbs the photosensitive spectrum light of the emulsifier layer for every emulsifier layer, and there is used a yellow pigment formation coupler on the blue-sensitive emulsifier layer, a magenta pigment formed

coupler for the green-sensitive emulsifier layer, and a cyan pigment formed coupler on the red-sensitive emulsifier layer. However, in response to the goal of the present invention, there may be used silver halide color photosensitive materials through a means that is different from the above-mentioned combination.

These pigment formed couplers do not expand the coupler that is considered to be a ballast group within the molecule, and it is desirable to have a group with a carbon number count of 8 or more. Furthermore, also when these pigment forming couplers are 4 equivalents, which are necessary to reduce the silver ions of 4 molecules, in order to form the pigment of 1 molecule, anywhere 2 equivalents may be found, there can be silver ion reduction for 2 molecules. With the pigment forming coupler, compounds exist that release beneficial fragments photographically such that according to the coupling of the oxide of the developing agent, there are image control agents, image promotion agents, developers, silver halogenized solvents, color suspension agents, hardeners, couplers, capry inhibitors, chemical sensitizes, and spectral sensitizers.

Among these, there is release of the developer control agent following development. The coupler, which improves

the freshness of the image and the granularity of the image, is called DIR coupler. In place of the DIR coupler, there may be used a DIR compound that releases a developer control agent at the time of generating a colorless compound through a coupling reaction with an oxide of the developing agent.

The DIR coupler that is used and the DIR compound have a direct control agent that is bound to the coupling site, and the control agent binds to the coupling site through a divalent group, and there is included an object (called timing DIR coupler and timing DIR compound) that the control agent binds so as to be released through an electron movement reaction within the molecule or a nucleophilic reaction within the molecule within the group that was separated by the coupling reaction. Furthermore, it is possible that the control agent uses the dispersed material after separation and also uses what was not dispersed independently or in combination by application. There is performed a coupling reaction with an oxide of the aromatic primary amine developer, and it is possible to use a colorless coupler that does not form a pigment (called competition coupler) in combination with a pigment forming coupler.

As for the yellow pigment forming coupler, it is possible

to use the well-known acyl acetanilide. Among these, it is beneficial to use the benzoil acetanilide and pivaloyl acetanilide series compounds.

As for the magenta pigment forming coupler, it is possible to use together, other than those mentioned with the present invention, 5-pyrazolon, pyrazoroben [UNKNOWN] coupler, open chain acetonitrile series coupler, and indazolon series coupler.

As for the cyan pigment forming coupler, phenol or naphthal series coupler is used.

Among the pigment forming couplers that do not require adhesion to the silver halide crystal surface, DIR couplers, DIR compounds, image stabilizers, color capry inhibitors, infrared ray absorber, and fluorescent whiteners, the hydrophobic compounds can be used to disperse by using a solid dispersing method, a latex dispersing method, or an oil drop emulsified dispersion method in water. These can be appropriately selected in response to the chemical construction of the hydrophobic compound such as capry. The oil drop emulsified dispersion method in water can use well-known conventional dripping methods that disperse the hydrophobic additives of the coupler and normally are dissolved by using water-soluble organic solvents with low melting points as necessary for

the organic solvents with boiling points in excess of 150 °C and/or dissolving by using water-soluble organic solvents and by using surfactants in hydrophilic binders of gelatin aqueous solution, a stirrer, using a dispersion means for the homogenizer, colloid mill, and flow jet mixer, and after emulsified dispersion, there may be added to the hydrophilic colloid liquid as a goal. After dispersion or at the same time as dispersion, a process may occur that eliminates at the same time as dispersion low boiling point organic solvents.

For high boiling point solvents, the following organic solvents with boiling points at 150 °C or above may be used: phenol derivatives that do not react with developer oxides, [UNKNOWN], ester phosphate, citric acid ester, benzoic ester, alkyl amide, fatty acid esters, and trimesic acid.

/10

Together with high boiling point solvents, there can be used low boiling point or aqueous organic solvents instead of the above list. As for the organic solvents that are substantially insoluble in water and have low boiling points, there are the following: ethylacetate, propylacetate, butylacetate, butanol, chloroform, carbon tetrachloride, nitromethane, nitroethane, and benzene, or

as for water-soluble organic solvents, the following can be cited as examples: acetone, methylisobutyl ketone, β -ethoxyethylacetate, methoxy glycol acetate, methanol, ethanol, acetonitrile, dioxazin, dimethylformamide, dimethylsulfoxide, hexamethylformamide, dimethylene glycol monophenol ether, and phenoxyethanol.

When the pigment forming coupler, DIR coupler, DIR compound, imide stabilizer, color capry inhibitor, infrared ray absorber, and fluorescent light sensitizer have acid groups of carbonic acid and sulfonic acid, it is possible to introduce them into hydrophilic colloids as alkali aqueous solutions.

Melt the hydrophobic compound in a solvent that has a low boiling point solvent singularity or a high boiling point, and for the dispersion agent when dispersing into water by using mechanical or ultrasound means, it is possible to use anionic surfactants, nonionic surfactant, cationic surfactant, and dual surfactants.

Using between the emulsifier layers of the photosensitive material (identical photosensitive layer between and/or different sensitive layers between), the electron movement agent or the developer oxide moves, and a color that is suspended is generated, because there is a color capry inhibitor that is used to prevent freshness deterioration,

and accentuated granularity, it is possible to use the color acpry inhibitor.

It is permissible that the color capry inhibitor contain an emulsified layer itself, and there is established an intermediate layer between adjacent emulsified layers.

As for the color capry inhibitor, it is desirable to use a hydroxynone derivative, aminophenol derivative, a gallic acid derivative, and ascorbic acid derivative. More specifically, the following are US Patents: /11

美国专利第2,380,290号、第2,328,327号、第2,403,721号、第2,418,613号、第2,675,314号、第2,701,197号、第2,704,712号、第2,728,659号、第2,732,300号、第2,735,765号、第2,700,453号、第50-92988号、第50-92989号、第50-93928号、第50-110337号、第50-156438号、第52-146235号、第55-95948号、第55-5247号、特公第50-23313号

It is possible with the sensitizing material that used the present invention's silver halide emulsifier, an image stabilizer that prevents pigment images.

As for the image stabilizer, it is desirable to use hydroquinone derivatives, gallic derivatives, phenol derivatives and its spiro body, hydroxyl [UNKNOWN], and its spiro body, piperidine derivatives, aromatic amine

compounds, benzodioxzian derivative, [UNKNOWN], [UNKNOWN] derivative, compounds containing silicon atoms, and thioether. More specifically, the following patents have been cited: English patent 1, 410, 846; Japanese Kokai Patents Showa 49-134326, 52-35633, 52-147434, 52-150630, 54-145530, 55-6321, 55-21004, 55-124141, 59-3432, 59-5246, 59-10539, Patents Showa 48-31625, 49-20973, 49-20974, 50-23813, 52-27534, US Patents 2, 360, 290; 2, 418, 613; 2, 675, 314; 2, 701, 197; 2, 704, 713; 2, 710, 801; 2, 728,659; 2, 732, 300; 2, 735, 765; 2,816, 028; 3, 069, 262; 3, 336, 135; 3, 432, 300; 3, 457, 079; 3, 57 3,050; 3, 574, 627; 3, 698, 909; 3, 700, 455; 3, 764, 337; 3, 935, 016; 3, 982, 944; 4, 013, 701; 4, 113, 495; 4, 120, 723; 4, 155, 765; 4, 159, 910; 4, 254, 216; 4, 268, 593; 4, 279, 990; 4, 332, 886; 4, 360, 589; 4, 430, 425; 4, 452, 884.

For the hydrophilic colloid layer for the protective layer and intermediate layer of the present invention's photographic-sensitive material, there is capry prevention by discharge whose cause lies in discharging through friction, and in order to prevent a deterioration due to the action of UV light on the image, there may be included an ultraviolet ray absorber.

In order to prevent deterioration of the magenta pigment forming coupler by formalin while preserving the

photographic-sensitive material, it is possible to use formalin scavengers.

When there is infrared or ultraviolet ray absorber in the hydrophilic colloid layer of the photographic-sensitive material, these may be color-fixed by a color fixer such as cationic polymers.

It is possible to add image promoters to the silver halide emulsifier layer of the photographic-sensitive material and/or other hydrophilic colloid layers and to add compounds that change the developer properties of the developer extender or bleaching promoter. The compounds that can be used and that are desirable as developer promoters are the compounds contained in items XXI B-D of RD17643. The developer extender is a compound contained in item XXI E of RD 17643. There may be used a developer promoter, and for other goals, a black and white developing agent, and/or their [UNKNOWN].

The photographic-sensitive emulsifier layer may contain, with the goals of increased sensitivity, improved contrast or developer promotion, polyalkylene oxide or its ether, ester or amine as derivatives, thioether compounds, thiomorpholino, 4 level ammonium compounds, urethane derivatives, urea derivatives, and imidazole derivatives. It is possible to use, for the photographic-sensitive

material, fluorescent bleachers with the goal of not obscuring the colors in the white color region, along with strengthening the white of the white region. As fluorescent light sensitizers, the compounds that can be used are contained in RD17643 item V.

There is established in the photographic-sensitive material a filter layer, a halation prevention layer, and a supplementary layer that prevents [UNKNOWN]. It is permissible that in these layers, and/or in the emulsifier layer, current flows out from the photographic-sensitive material during image processing or that there are dyes that bleach. For this kind of dye, it is possible to cite oxonol dye, melocyanine dye, cyanine dye, and azo dye.

It is possible to improve the silver halide emulsifier layer of the photographic-sensitive material and reduce the brilliance of the photographic-sensitive material in other hydrophilic colloid layers, and it is possible to add a matting agent with the objective of preventing photographic-sensitive material companions.

It is possible to add a smoother in order to reduce the irregularities in the photographic-sensitive material.

It is possible to add a charge inhibitor with the goal of charge prevention. The charge inhibitor may be used on the charge prevention side that does not laminate the

emulsifier of the support and may be used in the prevention of a colloidal layer other than the emulsifier layer on the side where the emulsifier layer is laminated for the emulsifier layer and/or support. The compounds that are preferably used as a charge inhibitor are the compounds that are contained in RD17643 X III.

It is possible to use various surfactants in the photographic emulsifier layer and/or other hydrophilic colloidal layers of the photosensitive material, with the goal of improving coating ability, charge prevention, smoothness, emulsified dispersion, adhesion prevention and photograph characteristics (developer promotion, hardening, and sensitizing).

The support that is used with the present invention's photographic-sensitive material is a possibly cured reflection support of laminated paper and synthesized paper such as olefin polymer (for example, polyethylene, polypropylene, ethylene/butane copolymers) and film that is comprised of cellulose acetate, cellulose sulfate, polyethylene, polyvinyl chloride, polyethylene terephthalate, and polycarbonate, polyamide and curable supports that establish a reflection layer on these films. After executing for the hydrophilic colloidal layer of the photographic-sensitive material, as necessary, corona

discharge on the support surface, ultraviolet ray bombardment, and flame processing, and there may be coating using 1 layer or more or an undercoat layer in order to improve directly adhesion of the surface of the support, charge prevention, dimension stability, abrasion prevention, hardening, halation prevention, friction properties, and/or other properties.

When coating the photosensitive material, it is good to use a thickening agent in order to improve the coating. In addition, in the same way as with the hardener, it is desirable to mix directly before coating by using a [UNKNOWN] mixer so that there is gelling before coating when adding beforehand to the coating liquid, in order to have a fast reaction.

A coating method is especially beneficial with extrusion coating and curtain coating, both of which can coat 2 or more layers simultaneously, and packet coating can also be used according to the objective. Furthermore, the coating can be arbitrarily selected.

The present invention's photosensitive material can be exposed by using electromagnetic waves of a spectral region in which the emulsifier layer that has formed the present invention's photosensitive material has sensitivity. The light source can use any well-known light source, such as

tungsten lamps, fluorescent lamps, mercury lamps, kerosene lamps, carbon arc lamps, xenon flush lamps, negative electrode ray tube flying support, every kind of laser light, light-generating diode light, and lamps that discharge from a fluorescent body that has been excited by electron beams, X-rays, gamma rays, and alpha rays. Exposure periods from 1 msec to 1 second can be used with the ordinary camera, and of course, it is possible to expose from 100 nanoseconds to 1 microsecond by using, for example, a negative electrode ray tube or xenon lamp, giving exposures less than 1 microsecond. It is possible to use exposures that are longer than 1 second. The exposure can also be continuous and may be performed intermittently. Well-known methods can be used for image processing of the photographic-sensitive material of the present invention. The processing temperature used has a range of from 18 to 50 °C, and corresponding to the goal, all forms of processing can be appropriately used as with black-and-white photo processing, i.e. (?) image processing all color photo processing that forms a color image. The developer agents that are used when doing black-and-white photo processing can be used independently or in combination with compounds such as dihydroxybenzene (for example, hydroquinone), 3-pyrazolidone (for example, 1-

phenyl-3-pyrazolidone), aminophenol types (for example, N-methyl-p-aminophenol), and ascorbic acid.

The developer liquid may contain well-known preservatives, alkali agents, pH (illegible), capry control agents, and furthermore, corresponding to the need, may contain dissolution agents, coloring agents, developer promoters, surfactants, bubble eliminators, hard water softeners, and hardeners.

Moreover, a developer agent can be contained in the photographic-sensitive material, and it is appropriate to use the present invention with film type sensitive material within the agent that is referred to as a type that processes in an alkali solution.

Next, when forming the pigment image, use an alkali aqueous solution that contains the generated color developer agent. The generated color developer agent can use well-known first-grade aromatic amino developers, for example, phenylenediamine.

The color developer liquid may include, in addition, pH mediators such as sulfite salt of alkali metals, carbonate, borate, and phosphate, halogen salt, and organic solvents such as organic capry inhibitor, hard water softener, [UNKNOWN], pentyl alcohol, ethylene glycol, and developer promoters such as quaternary ammonium salt and amine.

The processing after color processing is the normal bleaching processing. The bleaching liquid is used at the same time as the fixing processing, and may be done separately. Iron (II), cobalt (III), chrome (IV), and copper (II) are all multivalent metal compounds that may be used as bleaching liquid in addition to persulphates. For example, it is possible to use ferrocyanide, bichromatic salt, complex salts of iron and cobalt, ethylene diamine, tetraacidic acid, nitrolitriacetate, permanganate salt, etc.

[Embodiments]

Below, there is an explanation in further detail of the present invention by citing embodiments.

Embodiment-1

Chemically form a silver iodine bromide emulsifier that is comprised of silver bromide in addition to silver iodide 2.5 mol % to the maximum degree by using the silver and sulfur sensitization method to obtain a highly sensitive silver iodine bromide emulsifier.

Next, after dividing equally the emulsifier as shown below in Table 1, add the present invention's compound and comparative compounds, and further add in appropriate

amounts formalin as a hardener and saponin as a coating agent.

Obtain these emulsifiers by uniformly coating and drying so that the silver amount becomes 3g/m^2 on a polyester support. After letting stand 1 group of obtained experimental material in a refrigerator established at 5°C , another 2 groups were left in a high-temperature, low-humidity and high-temperature, high-humidity environments for 5 days; these 3 groups were wedge-exposed using normal methods. Next, after exposing at 20°C for 4 minutes using Kodak D-72 developer liquid, fixing, and washing, Table 1 shows the results.

The sensitivity in the table uses the reciprocal of the logarithm of the exposure amount necessary to obtain the capry concentration + 0.5 concentration, and shows as a relative sensitivity with 100 as the comparative material, and the capry values are shown using values that have subtracted a base concentration.

As is clear from Table 1, the compound related to the present invention is compared with the comparative compounds and controls capry generation by letting the materials stand under rigorous retention conditions. From the table it is understood that there was a reduction in sensitivity.

Table 1

Material No.	Capry inhibitor	Added amount	Unattended standing-3 days					65 °C, RH 5		
		(mg/Ag X 1 mol)	Capry	sensitivity	gamma	Capry	sens:			
1 (comparative)	nothing	-	0.14	100	2.9	0.30	86	2.4	0.20	89
		30	0.12	105	2.9	0.14	100	2.0	0.19	104
		300	0.10	100	2.8	0.11	93	2.7	0.10	100
2 (present invention)	illustrated-3	30	0.10	112	3.0	0.12	103	3.0	0.12	110
		300	0.08	102	2.9	0.09	100	2.3	0.09	102
		30	0.09	110	2.9	0.09	107	2.8	0.08	100
3 "	"	300	0.07	104	2.8	0.08	100	2.7	0.08	102
4"	illustrated-5	30	0.11	105	3.0	0.14	104	3.0	0.12	102
		300	0.08	100	2.9	0.11	102	3.0	0.10	100
		30	0.11	100	2.9	0.12	102	2.9	0.11	100
5"	"	300	0.08	100	2.9	0.10	97	2.8	0.09	98
6"	illustrated-8	12	0.13	100	2.9	0.27	90	2.4	0.20	92
		13	0.10	95	2.8	0.20	84	2.3	0.17	89
		150	0.14	100	2.9	0.30	85	2.7	0.20	90
7"	"	200	0.13	103	2.9	0.29	83	2.7	0.19	88
8"	illustrated-15									
9"	"									

10"	illustrated- 23	
11"	"	
12 (comparative)	[a]	
13"	"	
14"	[b]	
15"	"	

[Note] [a] 1-phenyl-5-mercaptotetrazol
[b] 4-hydroxy-6-methyl-1,3,3a,7-tetrazainden
(same for the following embodiments)

Embodiment-2

Prepare the material shown in Table 2 using the same emulsifiers as in Embodiment-1.
After wedge-exposing using normal methods after high-temperature and high-humidity processing in the same way the obtained material from Embodiment-1, and after developing at 35 °C for 35 minutes using the high-temperature, fast-developing liquid shown below, and after fixing and washing, the results showing sensitivity are presented in Table 2.

High-temperature, fast-developer processing method (using black-and-white photographic-sensitive material)

1-phenyl-3-pyrizoidon	1.5g	
hydroxynon		30g
anhydrous sodium sulfite		55g
potassium hydrate		30g
sulfuric acid		10g
potassium bromide		5g
5-nitroindazole		0.25g

glutaraldehyde (25% liquid)

5g

Add 1 quart of water.

Table 2

Material No.	Capry inhibitor	Added amount	Unattended standing-3 days						65 °C, RH 5	
		(mg/Ag X 1 mol)	Capry	sensitivity	gamma	Capry	sens:			
		-	0.17	100	0.92	0.24	91	1.30	0.22	94
16	nothing	10	0.10	97	1.25	0.21	98	1.24	0.19	97
(comparative)		200	0.16	93	1.30	0.23	94	1.28	0.20	98
		150	0.17	100	1.30	0.23	90	1.29	0.21	95
17 "	[a]	150	0.08	102	1.29	0.10	103	1.30	0.09	100
		150	0.09	100	1.29	0.11	102	1.27	0.10	100
18 "	[b]	150	0.09	107	1.27	0.11	100	1.28	0.10	103
19 "	[c]	150	0.10	103	0.28	0.11	108	1.29	0.09	107
20 (present invention)	illustrated-5									
21 "	" -7									
22 "	" -19									
23 "	" -22									

[Note] [c]... 5-nitrobenzimidazole

As is clear from Table 2, when maintaining the photographic-sensitive materials under rigorous conditions and developing at high temperatures and rapid rates using developing liquid meant for fast processing, the compounds related to the present invention, and comparing with comparative compounds, gamma deterioration of capry was stopped, and it is understood that there was an improvement in stability while maintaining the film.

Moreover, using materials 16, 19, 31, and 23 among the materials prepared for Embodiment-2, there were experiments for developability by capry inhibitors that were dissolved in the developing solution.

After processing the comparative material 19 with $1\text{m}^2/\text{Q}$ developer liquid, the results of developing comparative material 16, which did not contain any capry inhibitors, indicated that there was a slight decrease in sensitivity of 8%, by comparing with the processing done using fresh developing liquid, and no decrease in sensitivity was seen after processing in the same way the materials 21 and 23 that are related to the present invention.

Embodiment-3

Prepare multilayer color photographic-sensitive material 24 by establishing in order the compounds below on a cellulose triacetate film.

First layer: halation inhibitor
gelatin layer that contains black color colloid silver

Second layer: intermediate layer
gelatin layer

Third layer: red-sensitive, low-sensitivity emulsifier
layer

silver iodide bromide emulsifier	silver iodide: 5 mol %
	average particle diameter
0.5 μm	

	silver coating amount
...1.79g/m ²	

sensitizing pigment II	6 x 10 ⁻⁵ mol per silver 1 mol
sensitizing pigment II	per 1 mole silver
coupler-A	0.06 mol per silver 1 mol
coupler-C	0.003 mol per silver 1 mol

coupler-D 0.003 mol per silver 1 mol

tricresyl phosphate coating amount 0.3 cc/m²

Fourth layer: red-sensitive, high-sensitivity emulsifier layer

silver iodide: 4 mol %
average particle diameter

0.7µm

silver coating amount ...

1.4g/m²

3 x 10⁻⁵ mol

sensitizing pigment II 1.2 x 10⁻⁵ mol per silver 1 mol

coupler-F 0.0125 mol per silver 1 mole

coupler-C 0.0016 mol per silver 1 mol

tricresyl phosphate coating 0.2 cc/m²

Fifth layer: intermediate layer
same as Embodiment 2

Sixth layer: green-sensitive, low-sensitivity emulsifier layer

Silver iodide bromide emulsifier silver iodide: 4 mol %
average particle diameter 0.5µm

silver coating amount 1.0g/m²

sensitizing pigment III- 3 x 10⁻⁵ mol per silver 1 mol

sensitizing pigment IV - 1 x 10⁻⁵ mol per silver 1 mol

coupler- B 0.08 mol per silver 1 mol

coupler-M 0.008 mol per silver 1 mol

coupler-D 0.0015 mol per silver 1 mole

tricresyl phosphate coating amount 1.4 cc/m²

Seventh layer: green-sensitive, high-sensitivity emulsifier layer

silver iodide: 5 mol %
average particle diameter

0.75µm

silver coating amount ...

1.6g/m²

sensitizing pigment III 2.5 x 10⁻⁵ mol per

silver 1 mol	
sensitizing pigment IV	0.8×10^{-5} mol per
silver 1 mol	
coupler-B	0.02 mol per silver 1
mol	
coupler-M	0.003 mol per silver 1
mol	

tricresyl phosphate coating amount 0.8 cc/m^2

/16

Eighth layer: yellow filter layer

gelatin layer that contains yellow colored colloid silver
in gelatin aqueous solution

Ninth layer: blue-sensitive, low-sensitivity emulsifier layer

silver iodide bromide emulsifier	silver iodide: 6 mol %
	average particle diameter

0.70 μm .

silver coating amount ...

 0.5 g/m^2

coupler-Y 0.125 mol per silver 1 mol

tricresyl phosphate coating amount 0.3 cc/m²

Tenth layer: blue-sensitive, high-sensitivity emulsifier layer

silver iodide bromide emulsifier	silver iodide: 6 mol %
	average particle diameter

0.8 μm

silver coating amount ...

 0.6 g/m^2

coupler-Y 0.04 mol per silver 1 mol

tricresyl phosphate coating amount 0.1 cc/m²

Eleventh layer: preservation layer

Coat gelatin layer containing polymethylmetaacrylate particles (diameter 1.5 μ m).

For the couplers of every layer, add a coupler to the solution of tricresyl phosphate and ethyl acetate, and add as an emulsifier p-dodecylbenzene sodium sulfonate, and after adding heat to the solution, mix with added 10% gelatin solution and use as emulsified with a colloid mill.

Add to every layer, in addition to the above-mentioned

compounds, a hardener or surfactant.

Consider the material 24 as having been prepared in the way above.

The compound is used for making experimental material.

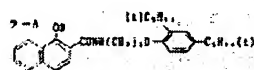
sensitizing pigment I: anhydro-5,5'-dichloro-3,3'-di-(γ -sulfopropyl)-9-ethyl-? pyrridium salt

sensitizing pigment II: anhydro-9-ethyl-3,3'-di-(γ -sulfopropyl)-9-4,5,4',5'-dibenzo? salt

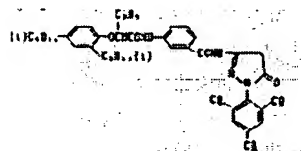
sensitizing pigment III: anhydo-9-ethyl-5,5'-dicholoro-3,3'-di-(γ -sulfopropyl)oxacarboyaninehydroxy sodium salt

sensitizing pigment IV: anhydro-5,6,5',6'-tetrachloro-1,1'-diethyl-3,3'-dichloro di (β -[β -(γ -sulfopropoxy)ethoxy]ethylimidazolocarbocyaninehydroxy sodium salt

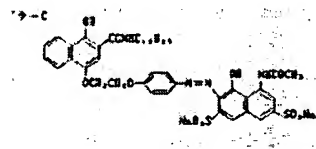
coupler-A



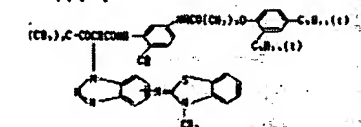
coupler-B



coupler-C

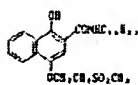


coupler-D



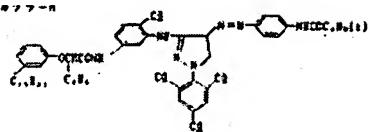
coupler-F

277-1



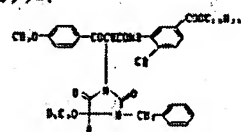
coupler-M

277-2



coupler-Y

277-3



/17

After adding all the sensitizing pigments for the red-sensitive layers of layer 3 and layer 4, which are the silver halide emulsifiers and the green-sensitive layers of layer 6 and layer 7, there is stabilization using well-known stabilizers by adding 3g of 4-hydroxy-6-methyl-1,3,3a,7-tetraiadine per silver halide 1 mol and 10mg of 1-phenyl-5-mercaptolazoil per silver halide 1 mol. The ninth and tenth layers of the next blue-sensitive emulsifier layer, before adding coupler-Y and after adding the compounds of the present invention found in Table 3 below, are laminate coated with the prepared material. After high-temperature, high-humidity processing for a maintained experiment of the obtained multilayered color photographic-sensitive material in the same way as with Embodiment-1, perform color processing after normal wedge-exposure.

Processing process (processing temperature 38 °C)

Processing Time

color developing	3 min 15 sec
bleaching	6 min 30 sec
washing	3 min 15 sec
fixing	6 min 30 sec
washing	3 min 15 sec
fixing	1 min 30 sec
drying	

In every process, the processing liquid composition that was used was the same as below.

[Color developer liquid]

4-amino-3-methyl-N-(β -hydroxyethyl)-aniline sulfate salt	
4.75g	
anhydrous sodium sulfite	4.25g
hydroxylamine 1/2 sulfate salt	2.0g
anhydrous potassium carbonate	37.5g
sodium bromide	1.3g
trisodium nitrilotriacetate salt	
2.5g	
potassium hydroxide	1.0g

Add 1 quart of water.

[Bleaching agent]

ethylenediamintetra iron ammonium acetate salt

100.0g
ethylenediaminetetra di ammonium acetate salt
10.0g
ammonium bromide
150.0g
glacial acetic acid
10.0g
Add 1 quart of water, adjust the pH to 6.0 using ammonium
water.

[Adhesive liquid]
thioammonium acetate 175.0g
anhydrous sodium sulfite 8.6g
meta sodium sulfite 2.3g

Add one quart of water, and adjust the pH to 6.0 using
acetic acid.

[Fixing liquid]

formalin (37% aqueous solution)

1.5ml

[UNKOWN] (KONISHIROKU PHOTO INDUSTRIES CO LTD)

7.5ml

Add 1 quart of water.

Table 3 shows the results of the preserving experiments on the blue-sensitive layer, and from these results, it is understood that the compounds related to the present invention had capry-control effects that did not give reduced sensitivity, with no daily deterioration in the photo's properties.

In addition, Table 4 shows the periods necessary for bleach processing, and from these results, it is understood that the compounds of the present invention do not deteriorate the desilvering compared to the comparative compounds.

Table 3

Material No.	Capry inhibitor	Added amount		Unattended standing-3 days						65 °C,
		(mg/Ag X 1 mol)		Capry	sensitivity		gamma	Capry		
		10 th layer	11 th layer							
24	nothing	-	-	0.41	100	0.59	0.63	89	0.57	0.55
(comparative)		-	30	0.30	98	0.64	0.50	89	0.62	0.48
25 "	[a]	15	15	0.27	95	0.67	0.47	87	0.64	0.40
		25	25	0.25	84	0.69	0.44	86	0.63	0.39
26"	"	150	150	0.40	100	0.60	0.60	90	0.58	0.50

27"	"	
28"	[b]	
29 (present invention)	illustrated- 13	
30"	illustrated- 13	
31"	illustrated- 13	
32"	illustrated- 16	
33"	illustrated- 16	
34"	illustrated- 16	
35"	illustrated 23	

Table 4

Material No.	Capry inhibitor	Added amount	Yellow concentration

		(mg/Ag X 1 mol)		Bleaching processing period	
		10 th layer	11 th layer	38 °C, 2 min	38 °C, 4 min
24 (comparative)	nothing	-	-	1.30	1.30
25 "	[a]	-	30	1.33	1.30
26 "	"	15	15	1.33	1.31
27 "	"	25	25	1.35	1.32
28 "	[b]	150	150	1.30	1.30
29 (present invention)	illustrated- 13	60	60	1.29	1.27
30 "	illustrated- 13	150	150	1.29	1.28
31 "	illustrated- 13	80	80	1.27	1.25
32 "	illustrated- 16	150	150	1.28	1.27
33 "	illustrated- 16	150	150	1.27	1.27

34"	illustrated- 16	
35"	illustrated 23	

[Effect of the Invention]

According to the present invention, as was clear from the above embodiments, even when placed under rigorous maintenance conditions, there was no generation of capry or reduction in sensitivity, no reduction in gamma, and no reduction in desilvering of the color photographic-sensitive material that was obtained as silver halide material, with no developer control from capry controlling agents that eluted in the developer liquid during development.

Applicant KONISHIROKU PHOTO INDUSTRIES CO LTD /19

Written Amendment

October 31, 1985

To: Japanese Patent Office

1. Subject matter

1985 Patent Application 164875

2. Title of the Invention

SILVER HALIDE PHOTOGRAPHIC-SENSITIVE MATERIAL

3. Person making the amendment

Relationship with matter	Applicant
Location	1-26-2 Nishi Shinjuku Shinjuku-ku Tokyo
Name (127)	KONISHIROKU PHOTO INDUSTRIES CO LTD
Representative Board of Directors	Ide, Satomi

Contact

1- Banchi Sakura-cho Hino Tokyo
KONISHIROKU PHOTO INDUSTRIES CO LTD (Tel. 0425-83-1521)

Patent Department

4. Date amendment requested

Voluntary

5. Amendment subject

Specification's "Detailed Description of the Invention"

6. Amendment Details

Make the following amendments for the detailed description of the invention

Page	Line	Before amendment	After amendment
56	8	sensitizing pigment II	sensitizing pigment I
56	10	for	3×10^{-5} mol with respect to
56	15	0.3cc/m ²	0.3ml/m ²
56	7	thioacetate	thiosulfate